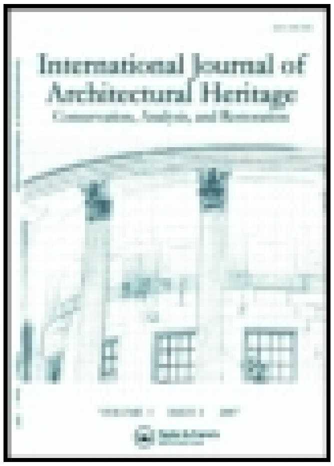

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Reaction to Fire of Existing Timber Elements Protected with Fire Retardant Treatments: Experimental Assessment

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REACTION TO FIRE OF EXISTING TIMBER ELEMENTS PROTECTED WITH FIRE RETARDANT TREATMENTS: EXPERIMENTAL ASSESSMENT

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Running Head - Fire protection of existing timber elements.

Abstract - Fire safety is an important issue of buildings safety**,** especially when their fire load contents enhance the risks of fire deflagration. When existing timber structures are involved, the most usual way to improve its reaction to fire is to treat wood with fire retardants. This study focuses on the surface protection of existing timber roof structures against fire, through the use of Fire Retardant (FR) treatments applied on site. An experimental investigation was carried out to study the effect of FR treatments on timber reaction to fire, with a special emphasis on timber members with biological deterioration and previously treated with preservative products. The behaviour and effectiveness of intumescent and non-intumescent treatments was also

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investigated. The study showed that the application of FR treatments improved the reaction to fire of timber, even in the presence of previous preservative treatments. However, the choice of the specific FR treatment should take into account the substrate conditions. Besides, test results suggest that protection systems involving multi layers (intumescent and non-intumescent) with different functioning modes each are likely to have a good global performance on the protection of timber elements against fire.

KEYWORDS - timber structures; structure fire; fire retardant treatments; intumescent; non-intumescent; rehabilitation.

1. INTRODUCTION

1.1. The need for fire protection

Fire safety is an important concern in all types of construction as fire deflagration endangers human beings and destroys patrimonial goods and historical values. Old urban centers generally present high fire loads and high risk of fire, due to commercial and industrial activities concentration, as well as abandoned buildings or deficient maintenance of buildings and their contents, which mainly enhances the risks of fire deflagration. Therefore, it is the contents of the building rather than the construction materials which provide the fire load. To mitigate these risks in the building, it's necessary to adopt safety measures such as prevention, detection and egress, and implement fire containment and extinguishment mechanisms (Coelho, 2008; Cruz and Santos, 2012).

When timber elements are present, it's necessary to retard the ignition of the combustible material and the flame propagation through it, by controlling either the source of heat or the contribution from combustible material itself, by modifying its reaction to fire.

The ignition and combustion of timber is mainly based on the pyrolysis (i.e. thermal degradation) of cellulose and the reactions of pyrolysis products with each other and with gases in the air, mainly oxygen (Hakkarainen *et al.*, 2005). Cellulose starts to pyrolyse in the temperature range between 260 °C and 350 °C (Russell *et al.,* 2007). The decomposition products either remain inside the material or, after being volatilized, are released as flammable gases. Gaseous substances react with each other and oxygen, releasing a large amount of heat that further induces pyrolysis and combustion reactions (Hakkarainen *et al.*, 2005). The decomposition products that weren't volatilized become char. The char formation will thermally and physically insulate the remaining timber (Sweet, 1993) by decreasing heat release rate and acting as a mass transport barrier for flammable gases released from the fuel and oxygen from the air (Lowden and Hull, 2013). As such, char formation gives large dimension timber excellent natural resistance to fire penetration (Sweet, 1993), depending on timber elements exposed area, compared with its cross section.

When the requirement is to protect timber and to minimize the losses caused by fire, timber is usually treated with fire retardant chemicals that improve its reaction to fire performance (although it remains flammable), particularly when aesthetic values need to be considered. The choice of fire retardant solution should be made taking into account its effectiveness, cost, application and end-use requirements, as well as possible side effects, including strength

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reduction, potential increase of metal fasteners corrosion, discoloration and physical alterations. Therefore, several factors must be considered, such as (Hakkarainen *et al.*, 2005):

- Type of wood based substrate;
- Regulatory requirements to be satisfied;
- New building or rehabilitation/reparation/maintenance/reinforcement;
- Service life conditions/environment;
- Installation conditions;
- Maintenance requirements;
- Effects, if any, on appearance or other natural or inherent properties of the substrate.

1.2. Fire retardant treatments for wood

Fire Retardant (FR) treatments for wood can generally be pressure impregnated into (new) solid wood or wood products, or applied as a surface treatment to timber products, or be added to wood based products during their manufacturing process. In **impregnation treatments**, timber is pressure impregnated with chemical solutions using pressure processes similar to those used for chemical preservative treatments (White and Dietenberger, 2010). However, considerably high retention of chemicals is necessary for FR protection. Penetration depth of chemicals into wood influences the FR protection that can be achieved and depends on wood species, wood internal structure, moisture content and the dimensions of timber elements.

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Pressure impregnation is considered the most reliable way to treat timber for new building projects, as a result of its high effectiveness and long term FR protection. The performance of pressure impregnation treatments is mostly dependent on the chemical properties of the FR product used (Hakkarainen *et al.*, 2005; IWS Ltd, 2011). Therefore, it is usually a better option than a surface treatment (see Table 1).

However, in certain situations, impregnation treatment is impractical (e.g. requires industrial equipment), expensive (like in the case of temporary construction), or impossible, as in the rehabilitation of existing timber structures, which must be treated in service (e.g. cultural heritage interventions). For these situations, the application of a **surface treatment** to timber elements is in general very easy to perform as it can be applied in situ. However, IWS Ltd (2011) mentioned that generally, FR surface treatments should only be used to improve fire performance of timber elements that are already in situ, because their maintenance requirements can be very difficult to monitor from a quality perspective.

In building rehabilitation situations, specific difficulties may be involved in the treatment of existing timber structures with FR surface treatments considering that timber is prone to biological attack and that these structures may contain certain features of cultural value that need be maintained. Cruz and Palma (2009) and Cruz and Santos (2012) presented an overview of these problems regarding that existing timber members may have surface carving or decorative coatings that should be maintained for their historical interest. Biological deterioration may also be found on existing timber members, and these may have a previous preservative protection or may require it. In such cases, decision is necessary regarding the possible need for removal of the altered/treated surface layer and/or the choice of suitable FR surface treatments concerning their efficiency and compatibility.

There are several literature reviews (White and Sweet, 1992; Russell *et al.,* 2007; Marney and Russell, 2008) about the combination of commercial fire retardants and preservatives (i.e. chemical systems) in order to protect wood against fire and biological deterioration. The ways to produce a combined FR and wood preservative treatment are (Marney and Russell, 2008):

- Modification of an existing preservative suitable for in-ground applications by the addition of a FR chemical;
- Chemical modification of wood using conventional FR that demonstrate good biocide resistance;
- The fixing into wood of conventional preservatives that demonstrate good fire retardance;
- Inorganic modification of wood to form wood-inorganic composites.

Although, Russell *et al.* (2007) observed that for a combined treatment to have a widespread acceptance amongst the treatment industry, it should be applied using conventional treatment technologies, most probably vacuum-pressure impregnation. Moreover, in those studies, the referred application process of the combined treatments is through timber impregnation. In Portugal, in building rehabilitation situations timber elements are mainly found as roof structures. In these old roof structures, it is common to find biological deterioration as a result of

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a widespread wood-boring beetle attack or local fungal or subterranean termites attack, namely in wet areas under the influence of eaves or singular points (Cruz, 2012).

Consequently, in the past, many roof structures were treated with oily products, aiming to reduce the water uptake of timber members, as well as to prevent biodegradation or to treat timber against it. The presence of these products may create particular difficulties for maintenance or rehabilitation interventions, independently of their effectiveness at the time of application. The visual assessment of timber quality and state of preservation may not be easy, due to the darkness and opacity frequently featured by these type of products. Their presence may also reduce the penetration of the new preservative treatment that may be required and, may also increase timber reaction to fire or jeopardize FR surface treatments efficiency (Laranjeira *et al.,* 2013). In these cases, it is imperative to know if the presence of previous treatments will change the performance of FR surface treatments, because it is not always possible to remove or avoid those treatments.

1.3. How fire retardant surface treatment improves fire performance of wood

1.3.1. Fire retardant mechanisms of action/protection

In a fire situation, FR solutions act by interfering with a particular stage of wood combustion process (i.e. during heating, decomposition, ignition or flame spread) through mechanisms and sub-mechanisms that may either act chemically and/or physically to inhibit or suppress wood

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combustion process. In order to make the treatment more efficient, some FR systems combine several mechanisms of action.

Therefore, the mechanisms of action to reduce combustion include (Hakkarainen *et al.*, 2005):

- **Changing the pathway of pyrolysis of wood**

This method is the most common and best known, usually referred to as the chemical theory, according to Browne (1958), Levan and Winandy (1990), Still *et al.* (1991) and Sweet (1993).

Most commercial FR for wood function by enhancing the pyrolysis reaction of cellulose through the pathway leading mainly to char formation. Therefore, FR components such as phosphorus and boron compounds reduce the burning of pyrolysis products and thus decrease the heat released by wood. It may also slow down pyrolysis reactions and stabilize the chemical structures of wood against decomposition.

- **Isolating surface layers**

Protecting the wood surface with an isolating surface layer delays the temperature rise and reduces the release of pyrolysis gases and the access of oxygen on the surface. These effects can be accomplished using intumescent surface treatments as they expand when temperature increases and form a thick, porous carbonaceous layer that will protect wood surface from fire.

According to White and Dietenberger (2001; 2010), an intumescent surface treatment incorporates three distinctive groups on the basis of it way of action: dehydrating agent, a blowing agent and a char former. While Hakkarainen *et al.* (2005) specifies it as the enhancing

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dehydration and esterification, enhancing intumescence and forming char substances. In turn, Wladyka-Przybylak and Kozlowski (1999) specifies four groups: dehydration agent, esterification catalyst, foam producing substance and carbonizing substance; and also, describes each process associated.

Luneva and Petrovskaya (2008) state that the mechanisms of chemical transformations in intumescent surface treatments under heating still remains to be understood, due to their complex composition and the fact that the main reactions occur at high temperatures. On the other hand, D'orazio *et al.* (2007) state that the physical properties of the intumescent surface treatments after the chemical reaction has occurred are not widely known.

Systems based on protecting the surface with an isolating intumescent treatment often include components that change the pyrolysis reaction.

- **Changing the thermal properties of wood**

The easiest way to make wood less combustible is to wet it: firstly, water changes the effective specific heat of wood as water has a higher specific heat than dry wood, and heating up and evaporating water consumes heat; and secondly, as water evaporating from wood surface reduces the combustibility of the mixture of air and pyrolysis gases.

FR components such metal hydrates act this way, due to their high thermal inertia and diffusivity, although a large amount of metal hydrates is needed for sufficient effects. As such, Lowden and Hull (2013) reported that they are rarely used in the protection of timber elements.

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- **Diluting pyrolysis gases**

The combustion gases evolved during pyrolysis may be diluted by gases released from FR, such as aluminium hydroxides releasing water vapor at temperatures just below the thermal degradation temperature or other FR solutions producing carbon dioxide or another non-combustible gas.

In the past, some FR acted by inhibiting the chain reactions in the gas phase combustion of wood as radical scavengers, such as halogen compounds. However, Östman *et al.* (2006) refer that halogenated compounds have been completely avoided mainly due to environment aspects, such as bioaccumulation in people and adverse effects in children (Lowden and Hull, 2013).

1.3.2. Fire retardant chemical classes and their side effects on timber elements

FR mechanisms of action depend on their chemical nature. However, besides fire performance improvement, FR application to timber may also develop secondary side effects as they retain moisture, reduce strength and increase the potential to corrode metal fasteners. The magnitude of the side effects depends on the FR chemical selection and application process (Levan and Winandy, 1990). Therefore, several studies have been developed over time aiming to find chemical formulations that minimize their side effects although, despite several efforts, the optimal formulas have not yet been found, according to Qu, *et al.* (2010).

The most common FR active chemicals are inorganic (Still *et al.* 1991; Qu, *et al.*, 2010; White and Dietenberger, 2010). These solutions include several phosphonates, boron based compounds and also carbonate and sulphate compounds (White and Dietenberger, 2001; Qu, *et* *al.*, 2010). The combination of these chemicals provides a fire performance improvement for wood and many of these combinations are available at different costs.

Inorganic FR solutions are used for timber interior applications due to their water solubility. When they are used in timber exterior applications or subjected to repeated cleaning actions, leaching becomes an issue as migration of the salts with the movement of water in wood takes place due to moisture content variation. In this case, the FR treatments lose effectiveness.

Timber treated with inorganic FR is usually more hygroscopic than untreated timber, depending on the retention of chemicals and timber elements dimension. This hygroscopicity is particularly high at high values of relative humidity, e.g. above 75 % relative humidity, according to Östman *et al.* (2001).

Water insoluble organic FR have been developed to meet the need for leaching resistant solutions and they include resins polymerized after impregnation into wood (an amino resin system based on urea, melamine, dicyandiamide and related compounds), and graft polymer FR attached directly to cellulose (White and Dietenberger, 2010).

The classes of active chemicals for common FR currently used for wood are (Russell *et al.*, 2007):

- **Phosphorus containing FR**

Phosphorus is usually the central element in FR for wood due to its particular effectiveness in materials with high oxygen content, such as cellulosic's (i.e. wood). Monoammonium phosphate and diammonium phosphate are two of the most effective FR components.

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Phosphorus containing FRs act on a burning situation in more than one way: they shield the condensed combustible layer (formed from the volatile flammable gases released during pyrolysis), thereby cooling down the condensed phase and inhibiting the access of oxygen and thus ignition. In addition, they form or help the development of a carbon char on the surface, thereby protecting the remaining condensed combustible layer from escaping into the flame and combining with oxygen to propagate the flame. Therefore, the reactions are: the FR is converted by thermal decomposition to phosphoric acid, which in the condensed phase extracts water from the pyrolysis substrate causing it to char.

Phosphorus compounds have the potential to increase the moisture content of wood in humid conditions, promoting fungal decay and so, they are more suited to interior applications where leaching is not an issue.

- **Nitrogen containing FR**

Melamine is the primary nitrogen containing FR used and rarely works well on its own. Thus, it is usually mixed with another FR component that enables the formation of a condensed phase to form char (e.g. phosphorus) or gas phase reaction to scavenge free radicals. FR systems based on melamine and derivatives are used in intumescent systems as they can enhance intumescence. Therefore, melamine-based FR frequently employs several mechanisms to wood flame retardancy - they also vaporize in a fire situation, thus diluting the fuel gases and oxygen near the combustion source. Besides melamine, melamine-formaldehyde resins, urea and dicyandiamide are other nitrogen compounds used in FR formulations.

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- **Combined phosphorus and nitrogen systems**

They are frequently used together in wood because they behave synergistically, i.e. the phosphorus acts to protect the burning surface by forming a char and the nitrogen is released as a gas and dilutes the combustible volatile products released from wood.

Luneva and Petrovskaya (2008) mentioned that, currently, phosphorus-nitrogen containing intumescent FR are most widely used for wood due to the effect of their composition on the protective action, water resistance of the formulations, and thermal decomposition and stability of phosphorus-nitrogen containing compounds in FR treated wood elements. Those authors developed an investigation to study new green intumescent FR for wood and to examine the effect of their composition on the protective action and water resistance. Therefore, they studied a phosphorus-nitrogen containing FR developed for wood, containing ammonium phosphate, a polyol, an organic amide, organometallic compounds and HW-1 dispersion and they concluded that this formulation provides high fire retardancy and high water resistance of treated wood.

- **Boron containing FR**

Boron compounds give a long-lasting protection due to their deep penetration into wood. Mixtures of borax and boric acid also impart preservative properties to wood as well as having a reduced impact on mechanical properties of wood compared to some other FR chemicals.

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- **Metal hydrates containing FR**

They act by cooling the fuel source and diluting the gases, and normally, they are required in large quantities to be effective. The most common metal hydrate used as a FR for wood is aluminium trihydroxide.

Table 2 presents an overview of the classes of active chemicals and potential mechanisms of action for common FR for wood, based on the review on these subjects.

In addition to the positive benefit of reducing the flammability of wood, FR treatments can have adverse effects on other important properties. FR chemicals may increase hygroscopicity (Holmes, 1977) and may cause reductions in mechanical properties.

Several studies about the side effects that FR solutions have on mechanical properties of timber elements have been developed over time and several hypotheses have been presented of why strength and stiffness reductions occur. Levan and Winandy (1990) present a literature review about the factors that influence the loss of strength on timber elements, such as: wood thermal degradation process; effect of acids present in the FR chemicals applied; effect of temperature on strength; and combined effect of FR chemicals applied and temperature on strength.

FR treatments are known for their potential to adversely affect the mechanical properties of the wood. Potential effects of the FR treatment include a simple reduction at the time of the treatment and drying process. Thus, it is essential that design recommendations for any reductions in the structural design values be obtained from the FR manufacturer for applications involving structural elements.

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The wood thermal degradation process of this time-dependent loss of strength is intrinsically related with temperature and relative humidity conditions of a roof that the FR solution is exposed to. Of FR chemicals examined, the more severe loss of strength due to elevated temperature exposures were with monoammonium phosphate or phosphoric acid (White and Sweet, 1992). Therefore, under the influence of continuous high temperature conditions, such as in roof applications (frequently, designated by thermal-induced degradation), a significant loss of strength occurs. Still *et al.* (1991) and Winandy *et al.* (1991) reported several cases of roof timber structures protected with FR solutions that suffer reductions in strength and performance within several years of installation in the typical environmental exposures of a roof.

As with earlier problems of hygroscopicity, ASTM (American Society for Testing and Materials) test methods were developed to identify those treatments that were prone to have time-dependent loss in strength in elevated temperature applications. These non-fire performance criteria are part of specifications for pressure impregnated FR treated wood (White and Dietenberger, 2010) that are designed to insure that the FR treated wood provide acceptable levels of performance.

Lebow and Winandy (1999) investigated the relationship between wood pH and the mechanical properties of FR treated plywood exposed to extended high temperature conditions. They observed that all plywood treated with FR that were studied showed a large and rapid decrease in PH, with the most rapid decreases occurring with formulations containing phosphoric acid. Thus, a strong relationship was identified between changes in pH of the plywood and reductions in their mechanical properties. The authors concluded that the pH of FR treated plywood is a good indicator of its current condition and may have potential as a predictor of future strength loss as the plywood is subjected to elevated in-service temperatures.

Anthony and Drerup (2011) presented an experimental investigation about mechanical properties of wood trusses connected with metal plates that were originally treated with monoammonium phosphate. The specimens were removed from a roof framing of a residential building after nearly twenty years of service and were mechanically tested in bending and tension, in accordance with applicable ASTM standards. The authors concluded that the FR treated wood removed from the building had approximately half of the expected strength for untreated wood of the same species. When they compared these results to previously published data for less aged FR treated lumber, they suggested that the strength loss is progressive over time rather than a simple reduction at the time of manufacture.

The application of FR treatments in timber elements with metal fasteners might cause their corrosion during the service life of the timber elements, as FR solutions are often either acidic or alkaline and likely to increase the timber higroscopicity. Corrosion of fasteners can thus be accelerated under conditions of high relative humidity (i.e. roof applications) and in the case of fire deflagration if corrosive gases or acids are released during the thermal degradation, according to Östman *et al.* (2001).

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1.3.3. Intumescent versus non-intumescent treatments

Fire retardant surface treatments for wood are in general easy to apply as they can be applied manually in situ through brushing, airless spray, paint roller or by immersion. They are rapid to perform, quite economical and they can consist of colorless products (e.g. intumescent varnish).

Surface treatments, generally, can be divided into two groups according to their way of operation (Hakkarainen *et al.*, 2005; White and Dietenberger, 2010): intumescent and non-intumescent treatments.

Intumescent treatments are usually varnishes or paints that, after drying, form a clearly visible film on the wood surface. These coatings are specifically formulated to, when exposed to high temperatures (i.e. temperatures lower than wood combustion temperature), chemical reactions take place and they will change into an expanded foam, providing protection to the underlying wood surfaces from fire. Generally, the foam layer expands by up to 200 times the coating volume, according to Russell *et al.* (2007). The foam layer is a good thermal insulator, fire resistant and have a low density.

In a first approach, through an experimental investigation of both the thermal conductivity and density of the expanded foam, D'orazio *et al.* (2007) reported that the creation of the multi-cellular structure originating from the gas production, which takes place as the chemical reaction occurs, is not at all completely deterministic, which may partly justify the different properties of the final product.

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Hakkarainen *et al.* (2005) mentioned that to obtain an adequate fire performance, it should be applied a relatively thick surface layer (a few hundreds of micrometers), corresponding to a consumption of the order of 500 g/m^2.

Intumescent treatments are mostly used to treat timber as they are usually very effective in inhibiting timber combustion and simple to apply. However, their drawbacks are high cost, a tendency to cover the appearance of wood and their application is limited to indoor end uses since they are strongly hygroscopic. Generally they involve the application of a topcoat due to film susceptibility to abrasion and wear. When applied, topcoat thickness must follow producer's recommendation, taking into account the foreseen end use conditions, such as potential cleaning of the protected surface, which could result in the loss of FR efficiency.

Non-intumescent treatments are substances similar to those used in pressure impregnation. When applied they do not form a film or distinctly change the appearance of wood surface. However, in order to perform an efficient FR surface treatment for wood, it is crucial to use chemicals specifically designed for surface treatments. Hakkarainen *et al.* (2005) reported that these treatments have an effect on pyrolysis mainly through chemical means. However, due to their slight swelling ability, they also can work partly through the physical phenomena described in intumescent treatments, but much less expanded.

ETAG 028 (2009), applicable to FR products incorporated (in situ) in construction products, also divides non-intumescent treatments in:

- **Surface impregnation treatment**

A surface impregnation treatment is defined as being a product in liquid or paste form that, when applied to wood, penetrates below the surface and, on drying or curing, deposits substances that impart FR properties to wood. The performance of such products depends on the combination of depth of penetration and amount of FR substances deposited.

- **Encapsulation coating system**

The complete application of an encapsulation coating system will encase wood surface to a thickness of at least 1 mm.

Table 3 presents the compounds most used in the formulations of intumescent treatments and some of the compounds used in the formulations of non-intumescent treatments, according to the performed literature review.

Laranjeira (2012) carried out a market survey about fire retardant surface treatments for wood in the Portuguese market. It was found that a wide range of intumescent and non-intumescent products are available in the national market and both are frequently named by *ignífugo*. Besides, both treatments can integrate a paint system (application of successive layers of different products with a painting scheme associated) or be applied as an individual product (also with a painting scheme associated). Therefore, the FR surface treatment selection may be a very difficult task to perform.

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1.3.4. How reaction to fire performance of wood construction products is assessed

The reaction to fire properties, such as ignitability (ease of ignition), heat release, flame spread (continuous series of ignitions) and smoke production, are most relevant for FR wood products considering that (Sweet, 1993; Mikkola, 2004; Hakkarainen *et al.*, 2005):

- When wood reaches the ignition temperature, as a result of heat flux distributions from flame or other sources, the flame propagation along wood surface takes place through a continuous series of ignitions;

- The higher the heat released from a wood product, the faster the flame spread;

- Smoke produced during a fire is mainly formed by carbon containing particles that reduce visibility. High smoke production in the early phases of a fire is very harmful, considering the risks for building users, because it endangers emergency egress through the reduction of visibility and the irritating and incapacitating effects of smoke gases.

From the point of view of the European regulations (Euroclass system) the reaction to fire performance of construction products shall be assessed regarding all these aspects. Therefore, the protection of wood with FR is expected to result in delayed ignition, reduced heat release rate (Figure 1), slower spread of flames and generally, reduced smoke production during a fire (Holmes, 1977; Sweet, 1993; Hakkarainen *et al.*, 2005; White and Dietenberger, 2010).

In building applications, reaction to fire performance of wood is regulated based on performance in standard tests and a classification system (the European classification system or Euroclass

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system) in order to get the CE-mark, which is the official mandatory mark to be used for all construction products on the European market.

The Euroclass system consists of two sub-systems, one for construction products excluding floorings (mainly wall and ceiling surface linings), and another similar system for floorings (Östman and Mikkola, 2006, 2010; EN 13501-1, 2007; Santos, 2011). Laranjeira (2012) presents an overview of the Euroclass system.

The construction product location in a building (ceiling, wall, floor) is of great importance when fire safety engineering methods are used to analyse the safety of a building as a whole. Ceilings and upper parts of walls are always more critical in fire situations than lower parts in a building, as a result of rising fire propagation, generally through ceilings and upper parts of walls. Thus, in a fire risk analysis it is essential to take into account the overall layout of wood products in constructions. Therefore, the main principle in the Euroclass system is that all construction products have to be tested in conditions representing their intended end uses, because the construction product of concern may respond to fire in quite different ways depending on the end use conditions.

Wood properties that affect reaction to fire performance, such as density, thickness, joints and types of end use application, have been studied thoroughly and are included in the Euroclass system (Mikkola, 2004; Östman and Mikkola, 2006, 2010).

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1.4. Aim and program of work

Following the previous considerations, it seems that there is a lack of literature about fire retardant surface treatments behaviour when applied on existing timber members, i.e. with biodegradation and/or with previous preservative treatments or situations that may require the application of preservative protection.

Therefore, an experimental investigation was carried out in order to determine the effects of FR surface treatments on the combustion properties of Maritime pine (*Pinus pinaster*, Ait.) with biological deterioration and with previous treatments situations, which are often found in buildings rehabilitation in Portugal, as Maritime pine is widely used in building construction from the mid-nineteenth century (Machado *et al.*, 2009).

Besides that, another objective was established by the authors: to compare the behaviour and effectiveness of the intumescent and non-intumescent treatments, aiming to better understand the advantages and disadvantages of each surface treatment, regarding the protection phenomena when affected by fire, and also, ranking the different treatments tested.

To accomplish the objectives established, this study (Laranjeira, 2012) included old timber members from an existing roof structure attacked by wood-boring beetles and surface treated with an oily dark product quite common of timber that remain in service in a rehabilitation situation; and also new timber members (without biological deterioration), representative of timber elements introduced to replace seriously damaged ones. Both situations considered the possible application of a current surface preservative treatment.

The fire performance of timber untreated and treated with FR treatments was investigated by performing the radiant panel test (EN ISO 9239-1, 2010) in the first instance. Those FR treatments that showed a better performance were subsequently tested in the Single Burning Item (SBI) test (EN 13823, 2010). This approach is justified by the much easier radiant panel test as compared to the SBI, due to the test procedure and specimen size, despite SBI test be considered more representative of the end use application given to wood structures. Besides, the main purpose of the test program was not the classification of FR treatments, but it aimed to experimentally observe the mode of action of different FR treatments and to compare the response of different timber substrates and of timber protected with different products. The test program chose to cover a wide range of variables, rather than having a larger number of replicates for each test. Therefore, this approach was considered acceptable.

2. MATERIALS AND METHODS

2.1. Tested materials

2.1.1. Timber and test specimens preparation

In order to accomplish the purposes described above, several substrate conditions usually found in buildings' rehabilitation were considered (Table 4). All treatments studied were applied to Maritime pine timber (*Pinus pinaster*, Ait.). The timber specimens' with (inactive) biological attack by wood-boring beetle were collected from a demolished roof truss and existing floor boards. The roof truss evidenced previous treatment (an oily product on the surface).

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The radiant panel test specimens' dimensions (T x W x H) were 20 mm x 230 mm x 1050 mm, in accordance with EN 13238 (2010) and EN ISO 9239-1 (2010). To achieve the required width (230 mm), specimens were made by two boards joined along their length, with tongue and groove cuts held in place with staples driven from the unexposed face to fire. The SBI test specimens' dimensions (T x W x H) were 20 mm x 450 mm x 1200 mm for the vertical long wing and 20 mm x 150 mm x 1200 mm for the vertical short wing, both forming a right-angled corner. Vertical joints were provided (like in the radiant panel test specimens) to reach the defined long wing width.

A special emphasis was put on the even distribution of wood defects and biological attack amongst all specimens (Laranjeira, 2012).

Test specimens representing the old wood with attack by wood-boring beetles and treated with oily product at the surface (CO) were taken from the old trusses. These specimens contained the exterior faces of the old truss members, keeping the oily surface treatment.

The radiant panel test specimens CL and CI representing the old wood with attack by wood-boring beetles were taken from the old trusses, but were cut 2 cm away from the originally treated timber surface. The SBI test specimens CL representing the old wood with attack by wood-boring beetles were taken from floor boards, due to the shortage of truss material, but the tested surface was the unexposed (uncoated) side during the floor service life.

Test specimens SL and SI were obtained from new timber that was bought from a Portuguese wood supplier.

Moisture content was 12.6 ± 0.5 % for the timber from the roof truss and 12.4 ± 1.1 % for the floor boards, determined in accordance with NP 614 (1973). For the new timber 12.5 % moisture content was estimated since all the timber had been conditioned in the same room for a long time.

Test specimens from old timber (CO, CL, CI) were cleaned with an air compressor and test specimens from new timber (SL, SI) were sanded for surface preparation.

An insecticide organic preservative product available in the Portuguese market was applied (to CI and SI specimens) following the product specification (474 g/m^2, applied by brush in 3 coats, each one applied before drying the previous layer).

2.1.2. Fire retardant treatment

A survey of FR treatments available in the Portuguese market was performed, as described elsewhere (Laranjeira, 2012). Five FR treatments were selected for the experimental investigation, which included paint systems (a set of products to be combined within a painting scheme) and individual products, both covering intumescent and non-intumescent treatments: an *ignífugo* impregnation product (P1), an *ignífugo* varnish (P2), an intumescent product (P3); and two paint systems, one of them with intumescent protection (P4) and the other with intumescent and *ignífugo* protection, according to the producers definition.

Table 5 presents some technical specifications of the FR treatments studied and their total cost per unit area of protected timber. All FR treatments were applied by brushing according to the producers recommendation (although P1 treatment is meant as an impregnation product),

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following the specified amount per unit area. The amount applied was controlled by weighting each specimen on a digital scale (before and during each application). After treatment, test specimens were stored for at least 20 days in a ventilated room to allow the evaporation of solvents.

In order to characterize the chemical nature of the FR solutions selected, the Fourier Transform Infrared (FTIR) technique was used, since it allows the identification of the specific active components present in each product selected. This analysis was performed in two steps.

Firstly, each product was applied on a glass panel and left to dry or cure for 1 month. After that, each product sample was obtained by scratching the product on the glass surface; it was mixed with dry spectroscopic grade potassium bromide, and pressed into 13 mm diameter pellets for FTIR spectra analysis.

Silva *et al.* (2011) observed that when FR treatments (particularly, intumescent) are subject to high humidity environments, the solutions can lose the components responsible for the intumescent process. Therefore, to complement the first analysis, a portion of each fully cured product obtained (except sample P1 that behaves like a salt) was immersed in demineralised water, in a room at 23±3 ºC for two weeks. The resultant water was filtered and left to evaporate in a Petri dish until a dry residue was obtained. The dry residues obtained were crushed, mixed with dry spectroscopic grade potassium bromide, and pressed into 13 mm diameter pellets for FTIR spectra analysis.

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The FTIR spectra analysis was carried on a Bruker Tensor 27 spectrophotometer with a DLATGS detector, in the range of 400-4000 cm^{-1}. Thirty two scans were collected and averaged at a spectral resolution of 4 cm^{-1}. Table 6 presents the FR active components identified in the FR treatments selected.

Table 7 presents the FR treatments designation by their producers, and in accordance with ETAG 028 (2009), based on the dry film thickness obtained for the radiant panel test specimens. The results obtained show that the P2 treatment doesn't form a film thickness of at least 1 mm, therefore, it isn't an encapsulation coating system according to ETAG 028. Its classification as surface impregnation treatment is a possibility even though it formed a film thickness. P1 treatment is clearly a surface impregnation treatment since it doesn't form a film thickness. Significant differences were not observed between film thickness of the products applied on sound new wood specimens and old wood specimens with biological attack and with previous treatments (i.e. insecticide, oily product).

It should be mentioned that the test specimens were not conditioned to constant mass in accordance with EN 13238 (2010), because these conditions (23 ºC, 50 % RH) would lead to timber moisture content values much lower than those usually found in roof structures. For this reason, and also due to the small number of test specimens for each situation considered and to the adaptations performed in test conditions, the results obtained are not to be considered for the purpose of products classification.

2.2. *Test methods*

Tests have been performed in the Reaction to Fire Testing Laboratory (LERF) of the National Laboratory for Civil Engineering (LNEC).

The two tests of the Euroclass system performed were the radiant panel test (EN ISO 9239-1, 2010) and the Single Burning Item (SBI) test (EN 13823, 2010), so the comparison of results given by both tests was also of interest.

2.2.1. Radiant panel test

The imposed radiant flux in EN ISO 9239-1 (2010) simulates the thermal radiation levels likely to impinge on the floor of a corridor whose upper surfaces are heated by flames or hot gases or both, during the early stages of a developing fire in an adjacent room or compartment under wind-opposed flame spread conditions.

The radiant panel test (EN ISO 9239-1, 2010) assesses the critical heat flux, which corresponds to the maximum flame spread distance along the length of the test specimen, when exposed to a radiant flux (which maximum correspond to 11 kW/m^2). Also, the smoke development during the test, which results from combustion, is recorded as the light transmission in the exhaust stack. The test principle is illustrated in Figure 2a. Note that, flame spread distances vary inversely with the critical heat flux.

For this study, two panels of fiber cement (a non-combustible product, by Classification Without Further Testing, CWFT) (Santos, 2011) were placed under the test specimen to ensure that thermal degradation would initiate from the face directly exposed to test radiation.

2.2.2. Single Burning Item (SBI) test

The SBI test (EN 13823, 2010) is used for construction products excluding floorings. The test is based on a fire scenario of a single burning item (e.g. a wastebasket), located in a corner between two walls covered with the lining material to be tested.

In the SBI test (EN 13823, 2010), it was assessed the heat production and the smoke production from the test specimen when exposed to direct flame attack and thermal radiation from the main burner placed at the bottom of the corner. The SBI test apparatus is shown in Figure 2.b.

For this study, it was decided to reduce the heat output from the standard 30 kW for 11 kW in the main burner, in order to have an imposed average heat flux on the directly affected area of the test specimen similar to the maximum heat flux imposed by the radiant panel test.

Details for mounting and fixing the test specimen in the SBI included the use of panels of fiber cement with standard dimensions, for the same reason that was included in the radiant panel test, and rock wool to fulfill the remaining space from the two vertical wings, which form a right-angled corner. Test specimen was mechanically fixed to the panel of fiber cement, with bolts as far away as possible from the main burner, and rock wool was fixed with staples to the panel of fiber cement. Both materials used are non-combustible products (by CWFT) (Santos, 2011). The SBI test setup is given in Figure 2.c.

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Table 8 presents all the combinations for substrate conditions and FR treatments studied in the radiant panel test and in the SBI test, and also the nomenclature adopted for each situation. The work has been performed in two steps, firstly 22 specimens were tested in the radiant panel and then, it was extended to the SBI test with 8 test specimens selected based on the performance obtained on the radiant panel test. This experimental investigation studied the reaction to fire of the FR treated wood and also, the fire performance of specimens without FR treatment (COP0, CLP0, CIP0, SLP0, SIP0).

The radiant panel test specimens protected with P4 treatment were performed without the previous application of primer, however the results evidenced the advantaged of including it. So, for SBI test specimens, the P4 treatment included the previous application of a primer.

In order to measure the specimens' charred wood area resulting from the radiant panel test, specimens were cut in slices (10 cm in length) and the remaining cross-section was assessed by the Image tool program (Compdent.uthscsa.edu/dig/itdesc.html).

3. RESULTS AND DISCUSSION

3.1. Global assessment of the fire retardant treatments

The results indicate that the FR treatments application reduce considerably the reaction to fire of wood through the reduction of heat release (Figure 3), flame spread distance (Figure 4) and smoke production (Figure 5), as well as they increase the incident heat flux required to maintain flame as flame spread distances vary inversely with the heat flux.

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3.2. Substrate conditions effects

The results indicate (Figure 4) that the attack of wood by the wood-boring beetles (CLP0', CLP0'') doesn't increase significantly the wood reaction to fire, on its own, despite the increased specific surface area, when compared with new wood (SLP0', SLP0'').

The application of the studied insecticide on its own did not produce consistent effects (compare SLP0'-SLP0''-SIP0). But there is a clear trend for the specimens with insect damage and the insecticide or the oily product to have a poorer performance than clear sound wood.

The presence of previous treatments with the oily product increases fire degradation (COP0 in Figure 4) as well as smoke production (COP0 in Figure 5), which reduce the potential effectiveness of the FR treatments applied (Figures 4 and 5). However, even in the presence of damage from biological attack and previous preservative treatments, the ability of the FR treatments tested to provide protection is very significant.

Therefore, the results indicate that in the rehabilitation of existing timber elements, which will remain in service, if timber contains a previous treatment of an oily product, generally, it would be better for the reaction to fire performance of timber, to remove those oily substances before the treatment with FR (Figure 5). This will also be a good option when the application of an insecticide it's necessary (Figure 4).

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3.3. Comparative performance of the fire retardant treatments

The results in Figure 4 indicate that some of the FR treatments tested were more sensitive to the substrate conditions than others considering that their effectiveness were clearly reduced (e.g. P4 treatment), when applied to different substrates than clean new timber.

The treatments that included a primer, an undercoat with FR properties and a topcoat, seem to be generally less sensitive to the substrate conditions (Table 9). It's the case of the P5 treatment, which seems to be the most versatile protection studied due to its higher compatibility with the previous treatments applied on timber.

Figure 6 shows that treatment P5 has developed a more pronounced intumescent layer on the surface, when compared to intumescent treatments P3 (with just 6 % less of the amount applied, Table 5) and P4 (67 % less of the amount applied, Table 5).

It's interesting to note that P5 primer has a FR component (Table 6), which contributes to the reaction to fire protection of timber, possibly, by changing the pathway of pyrolysis of timber and/or isolating the surface layers (Table 2). Table 3 also specifies that this component takes part in the intumescent process of timber protection. Note also that, the P5 treatment leads to an intumescent and *ignífugo* protection, according to the producer's definition (Table 7). Therefore, possibly, the combination of multiple layers (intumescent and non-intumescent) with different modes of action appears to lead to a higher efficiency of the FR protection through the creation of synergisms.

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Despite both P1 and P2 treatments have been classified as surface impregnation treatments (Table 7), it's clear that P2 works differently from P1 (Figure 6), because P1 is clearly a surface impregnation treatment that does not form a film as already observed. Additionally, their chemical formulation is also different (Table 6).

As can be observed in Figure 6.b, the P2 treatment seems to have developed only a slight layer swelling, which leads its identification as non-intumescent treatment, considering the information available in the literature review.

Despite the versatility demonstrated by intumescent treatment P5, the application of intumescent treatments seems to require higher product amounts, generally with higher costs per protected wood surface (the most versatile treatment (P5) has a product consumed cost of about 8/10 of the most expensive one (P3)), as well as longer periods of workmanship (Table 5). However, one of the non-intumescent treatments tested (P1) resulted in an outstanding improvement of reaction to fire (Table 9) with a product consumed cost of about 1/10 of P5 (Table 5). This suggests that price and efficiency are not always directly related.

Table 9 evidences that in those surface treatments that include the application of a primer (e.g. P4), primer elimination may lead to a loss of efficacy, possibly, as a result of a higher intumescent undercoat absorption in the wood surface, which leads to a thinner intumescent layer.

Figure 7 indicates that intumescent treatments (P3, P4, P5) showed higher capacity to minimize losses of charred sections, being therefore advantageous in situations where it is desirable to ensure interior thermal insulation of the timber structural members.

Wladyka-Przybylak and Kozlowski (1999) studied a few intumescent treatments with different chemical formulations, which included pentaerythritol, dextrin, urea, dicyandiamide and monoammonium phosphate. They exposed horizontally Maritime pine wood to a heat flux of 35 kW/m^2 and to an external ignition source for 30 min. Some of the chemical formulations (dextrin, urea, dicyandiamide, monoammonium phosphate) showed fire retardant and heat-insulating properties by reducing heat release rate, mass loss rate, total heat released and effective heat of combustion for wood covered with such treatments, in comparison with untreated wood. Besides, for some of the chemical formulations the maximum heat release rate occurred at the test beginning, like it was observed in SBI specimens with P5 treatment (Figure 3). The others recorded a delay in the maximum heat release rate.

Leisted *et al.,* (2011) studied the application of two FR treatments (Flamol A and Burnblock, this one composed by ammonium phosphate, citric acid and sodium benzoate) into chipboard by smeared them with a small spatula to ensure that the liquids were equally distributed, and then exposed them to a heat flux between 8 and 80 kW/m^2 in a cone calorimeter test. The results demonstrated that Flamol A led to a reaction to fire improvement by increasing the ignition time, the critical heat flux to obtain ignition as well as reducing the heat release rate and effective heat of combustion, compared to untreated test specimens. The other FR presented minor or none reaction to fire improvement. Additionally, those authors made some observations on the

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charring of the chipboard samples and they observed that the untreated and the Burnblock treated samples look very similar on the surface after heat exposure as the cracks covered the entire exposed surface and made a pattern that can be compared to groups of small islands separated by the cracks itself. Flamol treated samples evidenced cracks in a more concentrated way around a specific area, rather than spread over the entire surface like the Burnblock treated and untreated samples. Therefore, they remarked that the charring of the test samples indicate that the FR among other effects prevents large surface cracking of the samples. A similar behaviour was also evident in P5 treated specimens in the present study.

IWS Ltd (2011) tested wood products (plywood, OSB, chipboard) protected with Intelligent Wood Systems – Fire Retardant (IWS-FR system) to fire attack using the cone calorimeter test and the single burning item (EN 13823, 2010). They concluded that the application of IWS-FR system reduces ignitability, fire propagation, flame spread as well as generated heat that provides extra time to escape the site. The IWS-FR system was applied using an impregnation process.

Therefore, previous studies prove there are significant differences between different FR treatments available in the market, their functioning mode and efficiency, as observed in this study. It is however remarkable the lack of published information regarding the influence of substrate conditions on the reaction to fire of FR protected wood, namely on the influence of biological attack and previous preservative treatment, although these may clearly have a significant effect on the FR performance and efficacy.

4. CONCLUSIONS

The following conclusions concern the tests performed and the tested treatments. Their extrapolation should be made with precaution regarding the small number of test specimens for each situation, enabling to investigate a large number of variables.

The experimental investigation was performed in two steps, firstly radiant panel tests for a wide range of variable combinations (of substrate conditions with Fire Retardant (FR) treatments) followed by Single Burning Item (SBI) tests for some selected combinations. This approach was validated by the similar response to both tests obtained for similar material (previous oily treatment and application of protection treatments P1 and P5) and the same ranking of the tested treatments obtained in both reaction to fire tests.

This experimental investigation confirmed that FR surface treatments can improve the reaction to fire properties of wood, by reducing heat release, flame spread distance and smoke production, as well as increase the incident heat flux required to maintain flame. Therefore, all the FR treatments tested improve the performance of wood in terms of reaction to fire. However, it was shown that some of these treatments seem to be more sensitive than others to the substrate conditions. Therefore, **particularly in a rehabilitation intervention, the choice of the FR treatment must be made in accordance with the substrate conditions present**, considering that:

- The substrate conditions of timber elements must be identified before the choice and application of FR treatments, as decision is necessary regarding the possible need for removal of

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the altered/treated surface layer or the need to perform efficiency/compatibility tests of suitable FR treatments;

- It was found that the efficiency of some treatments was seriously affected if applied on other substrates than clean new timber, whereas others seem to be far less sensitive to substrate conditions, thus being an interesting alternative whenever the old timber surfaces are to be maintained and/or preservative treatment can't be avoided. The FR paint systems (primer, undercoat with FR properties and a topcoat) seem to be generally less sensitive to the substrate conditions. Besides, the combination of multiple layers (intumescent and non-intumescent) with different modes of action appears to lead to a higher efficiency of the FR protection.

REFERENCES

Anthony, R. W. and Drerup, M. J. 2011. Investigation of the role of fire retardant treatment in the failure of wooden trusses. *SHATIS'11 International Conference on Structural Health Assessment of Timber Structures*. Lisbon.

Browne, F. L. 1958. *Theories of the combustion of wood and its control - a survey of the literature*. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory. Rep. No. 2136.

Chou, C.-S., Lin, S.-H., and Wang, C.-I. 2009. Preparation and characterization of the intumescent fire retardant coating with a new flame retardant. Advanced Powder Technology, 20:169-176.

Coelho, A. L. 2008. Conversations (in portuguese, *Conversas*). Construction (in portuguese, *Construção*) Magazine, 27:4-7.

Cruz, H. 2012. Inspection and monitoring of wood structures (in portuguese, *Inspecção e monitorização de estruturas de madeira*). *Symposium on Wood Roofing* (in portuguese, *Seminário sobre coberturas em madeira*), 43-54. Guimarães.

Cruz, H. and Palma, P. 2009. Fire protection of old timber roofs. Wood Science Research Needs. *COST IE 0601 Conference*. Hamburg.

Cruz, H. and Santos, C. A. 2012. Fire protection of wood structures (in portuguese, *Proteção ao fogo de estruturas de madeira*). Construction (in portuguese, *Construção*) Magazine, 51:36-37.

D'orazio, M. C., Corcione, M., and Fontana, L. 2007. Experimental characterization of the thermal behavior of intumescent paints. In *Proceedings of the 4th WSEAS International Conference on Heat and Mass Transfer*, 17-19. Queensland, Australia.

ETAG 028. 2009. *Guideline for european technical approval of fire retardant products.* Kunstlaan 40 Avenue des Arts. B - 1040 Brussels.

EN 13238. 2010. *Reaction to fire tests for building products - Conditioning procedures and general rules for selection of substrates.* CEN. Brussels.

EN 13501-1. 2007. *Fire classification of construction products and building elements - Part 1: Classification using data from reaction to fire tests*. CEN. Brussels.

EN 13823. 2010. *Reaction to fire tests for building products - Building products excluding floorings exposed to the thermal attack by a single burning item.* CEN. Brussels.

EN ISO 9239-1. 2010. *Reaction to fire tests for floorings - Part 1: Determination of the burning behaviour using a radiant heat source.* CEN. Brussels.

Hakkarainen, T., Mikkola, E., Östman, B., Brumer, H., and Piispanen, P. 2005. *Innovative eco-efficient high fire performance wood products for demanding applications. State of the art.* Sweden: Report for Vinnova-Tekes project InnoFireWood.

Holmes, C. A. 1977. Effect of fire-retardant treatments on performance properties of wood. Goldstein, I.S., ed. Wood technology: chemical aspects. In *Proceedings, ACS symposium series 43*, 82-106. Washington, DC: American Chemical Society.

IWS Ltd. 2011. *Enhanced fire resistance during construction - IWS-FR system for timber frame - Interim report.* Glenrothes: Intelligent Wood Systems Ltd.

Laranjeira, J., Cruz, H., and Santos, C. P. 2013. Fire performance of fire retardant treatments applied in existing timber structures (in portuguese, *Desempenho ao fogo de revestimentos retardadores de combustão aplicados sobre madeira de estruturas antigas*). Construction (in portuguese, *Construção*) Magazine, 53:50-51.

Laranjeira, J. P. Santos. 2012. *Reaction to fire of existing timber structures protected with fire retardant coatings* (in portuguese, *Reacção ao fogo de madeira antiga protegida com revestimentos retardadores de combustão*). Lisbon: Civil Engineering Master Thesis. Instituto Superior Técnico.

Lebow, S. T. and Winandy, J. E. 1999. Effect of fire retardant treatment on plywood pH and the relationship of pH to strength properties. Wood Science and Technology, 33:285-298.

ACCEPTED MANUSCRIPT

Leisted, R., Bengtsson, H., and Jomaas, G. 2011. *Experimental study of the effects of flame retardants applied to chipboard.* Lyngby: Bachelor Thesis. Technical University of Denmark.

Levan, S. L. and Winandy, J. E. 1990. Effects of fire retardant treatments on wood strength: a review. Wood and Fiber Science, 22(1):113-131.

Lowden, L. A., and Hull, T. R. 2013. Flammability behaviour of wood and a review of the methods for its reduction. Fire Science Reviews, 2:4.

Luneva, N. K. and Petrovskaya, L. I. 2008. Performance of intumescent fire retardant for wood. Russian Journal of Applied Chemistry, 81(4):704-707.

Machado, J. S., Dias, A., Cruz, H., Custódio, J., and Palma, P. 2009. *Assessment, conservation and enhancement of timber structures* (in portuguese, *Avaliação, conservação e reforço de estruturas de madeira*). Lisbon: Verlag Dashofer.

Marney, D. C. O. and Russell, L. J. 2008. Combined fire retardant and wood preservative treatments for outdoor wood applications - A review of the literature. Springer Science+Business Media, LLC. Fire Technology, 44:1-14.

Mikkola, E. 2004. Review of reaction to fire performance of wood based products. In *Proceedings of 8th World Conference on Timber Engineering*, II:325-330. Finland.

NP 614. 1973. *Wood - Determination of moisture content* (in portuguese, *Madeiras - Determinação do teor em água*). Lisbon: IPQ.

Östman, B. A.-L. and Mikkola, E. 2006. European classes for the reaction to fire performance of wood products. Holz als Roh- und Werkstoff, 64:327–337.

Östman, B. A.-L. and Mikkola, E. 2010. European classes for the reaction to fire performance of wood-based panels. Fire and Materials. DOI: 10.1002/fam.1054.

Östman, B., Tsantaridis, L., Mikkola, E., Hakkarainen, T., Belloni, K., Brumer, H., and Piispanen, P. 2006. *Innovative eco-efficient high fire performance wood products for demanding applications.* Sweden: Final report for Vinnova-Tekes project InnoFireWood. SP REPORT 2006:30. ISBN 91-85533-15-7.

Östman, B., Voss, A., Hughes, A., Hovde, P. J., and Grexa, O. 2001. Durability of fire retardant treated wood products at humid and exterior conditions - review of literature. Fire and Materials, 25:95-104.

Qu, H., Wu, W., Wu, H., Jiao, Y., and Xu, J. 2010. Thermal degradation and fire performance of wood treated with various inorganic salts. Fire and Materials. DOI: 10.1002/fam.1075.

Russell, L. J., Marney, D.C.O., Humphrey, D.G., Hunt, A.C., Dowling, V.P., and Cookson, L.J. 2007. *Combining fire retardant and preservative systems for timber products in exposed applications – state of the art review.* Australian: Forest and Wood Products, Research and Development Corporation. PN04.2007.

Santos, C. A. 2011. *The european classification of reaction to fire of construction products* (in portuguese, *A classificação europeia de reacção ao fogo dos produtos de construção*). Lisbon: LNEC Buildings (in portuguese, *Edifícios*) - ITE 55.

Silva, H. M., Rodrigues, M. P., and Cabral-Fonseca, S. 2011. Performance of intumescent coatings in high-humidity environments (in portuguese, *Desempenho de revestimentos intumescentes em ambientes de elevada humidade*). Corros. Prot. Mater., 30(3):85-91.

ACCEPTED MANUSCRIPT

Still, M. R., Levan, S. L., and Shuffleton, J. D. 1991. Degradation of fire retardant treated plywood: current theories and approaches. In *Proceedings of the International Symposium on Roofing Technology*, 517-522. Gaithersburg.

Sweet, M. S. 1993. Fire performance of wood: test methods and fire retardant treatments. Recent advances in flame retardancy of polymeric materials. In *Proceedings of the 4th annual BCC conference on flame retardancy*, 36-43. Stamford, CT. Norwalk, CT.

White, R. H. and Dietenberger, M. A. 2010. *Wood handbook, Chapter 18: Fire safety of wood construction.* General Technical Report FPL-GTR-190. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory.

White, R. H. and Dietenberger, M. A. 2001. Wood products: Thermal degradation and fire. In *Encyclopedia of Materials: Science and Technology*, 9712-16.

White, R. H. and Sweet, M. S. 1992. Flame retardancy of wood: present status, recent problems, and future fields. Recent Advances in Flame Retardancy of Polymeric Materials. In *Proceedings of 3rd Annual BCC Conference on Flame Retardance,* 250-257. Stamford, CT. Norwalk, CT.

Winandy, J. E., Ross, R. J., and Levan, S. L. 1991. Fire retardant treated wood: research at the Florest Products Laboratory. In *Proceedings of the International Timber Engineering Conference,* 4:69-74. London.

Wladyka-Przybylak, M. and Kozlowski, R. 1999. The thermal characteristics of different intumescent coatings. Fire and Materials, 23:33-43.

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Figure 1 – Heat release curves for untreated and Fire Retardant (FR) treated Douglas-fir plywood, 12.5 mm thick (White and Dietenberger, 2010)

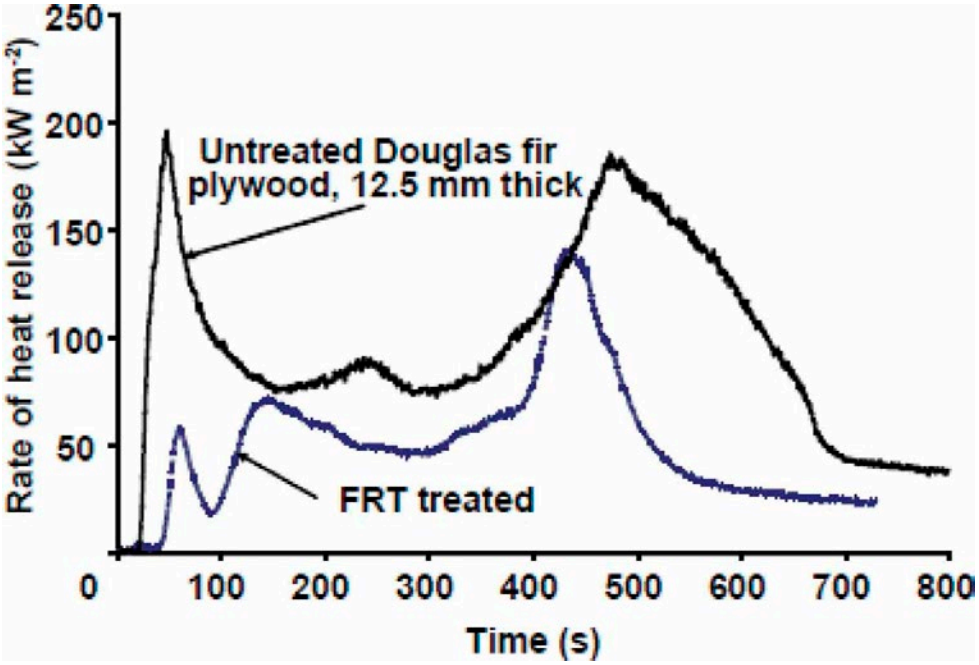

Figure 2 – a) Radiant panel test (for floorings) (EN 9239-1); b) The SBI test (EN 13823) (adapted from Östman and Mikkola, 2006); c) SBI test setup adopted (Laranjeira, 2012)

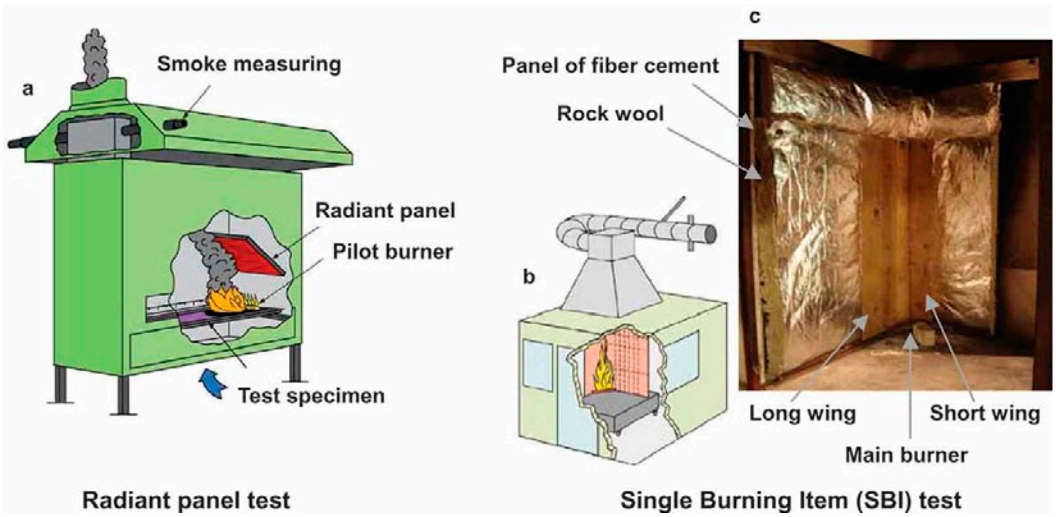

Figure 3 – SBI test – Average of the heat release rate (kW), (HRR_{30s}) (The average values presented correspond to a moving average of the heat release rate determined for each instant t considering the values recorded between t-15 s and t+15 s)

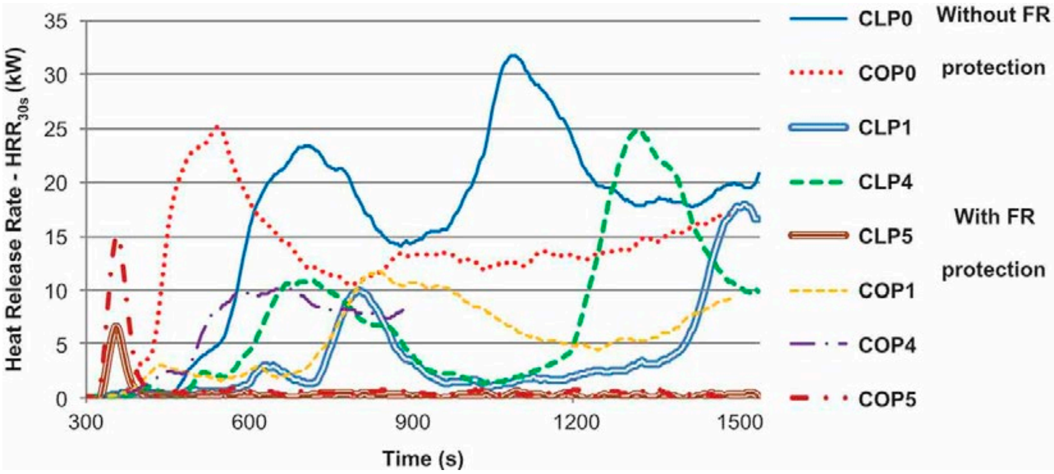

Figure 4 – Radiant panel test – Maximum flame spread distance (mm)

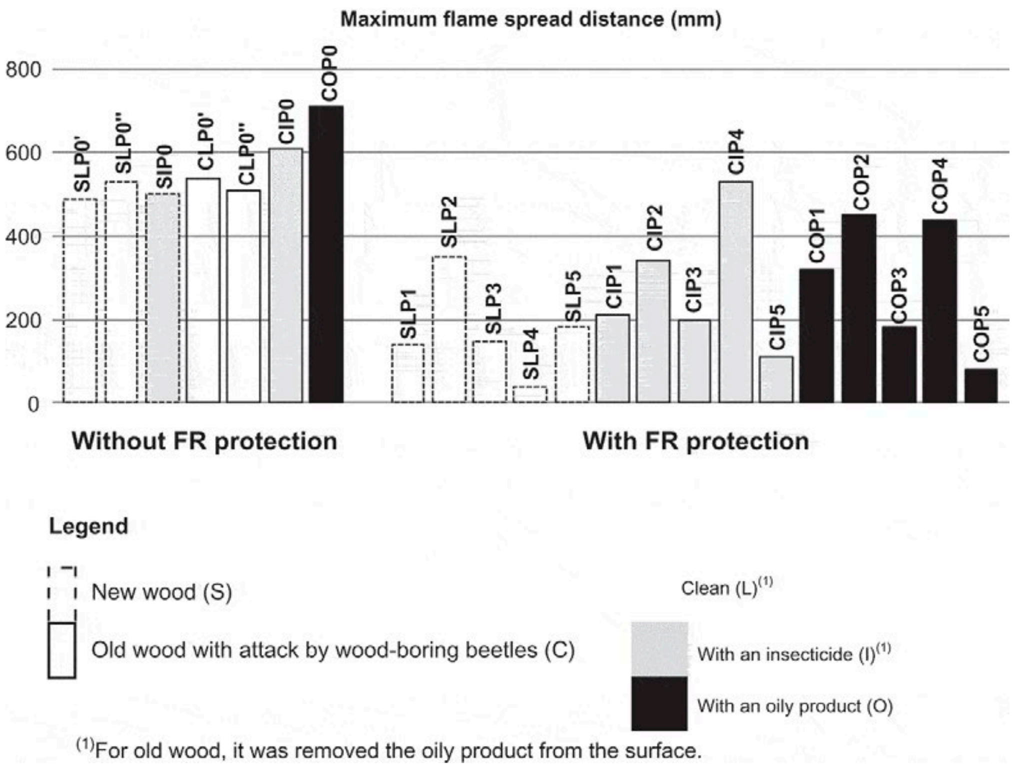

Figure 5 – SBI test - Total smoke production from the specimen in the first 600 s of exposure to the main burner flames (m^2), (TSP_{600s})

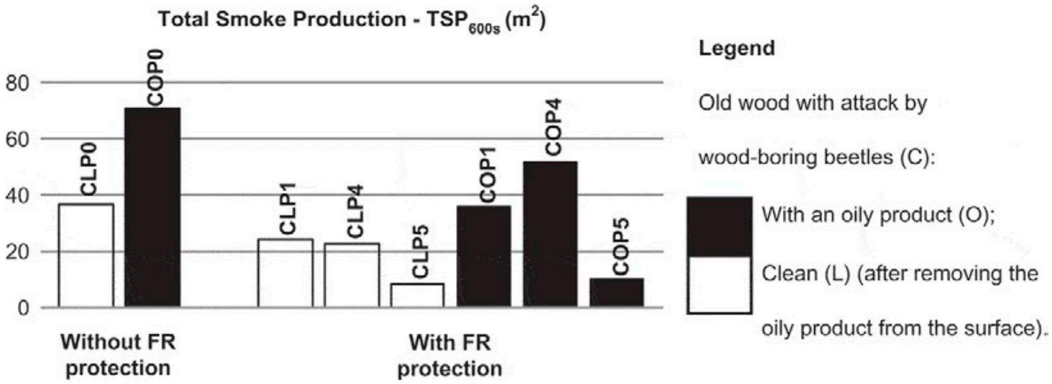

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Figure 6 - Radiant panel test - a) SLP1, b) SLP2, c) SLP3, d) SLP4 and e) CIP5

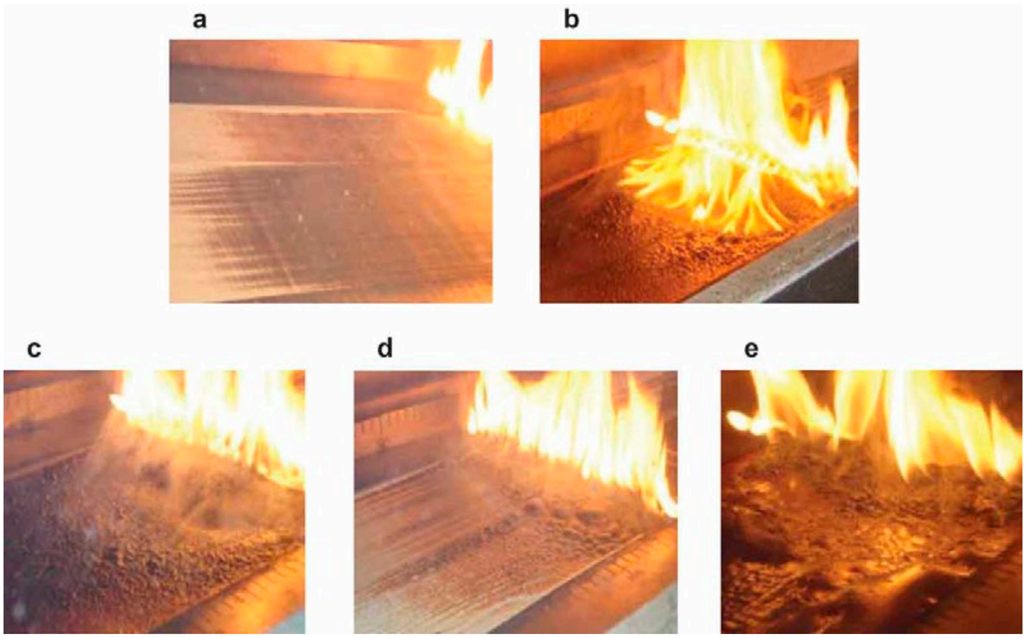

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Figure 7 – Normalized residual sections (in % of the initial section) of specimens tested in the radiant panel

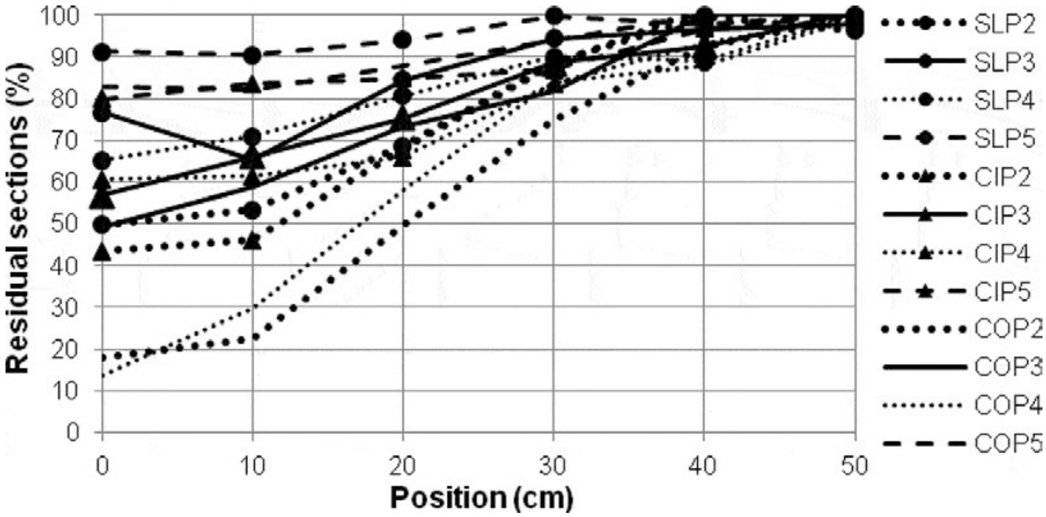

Table 1 – Potential advantages and disadvantages of Fire Retardant (FR) impregnation and surface treatments (adapted from Hakkarainen *et al.*, 2005; Russell *et al.*, 2007; White and Dietenberger, 2010; IWS Ltd, 2011)

Impregnation treatment	**Surface treatment**
Applied in factory	Applied in situ
Higher control and traceability of application conditions	Potentially less control and traceability of application conditions
Impregnation of all faces	Applied only on accessible faces
Potentially high penetration depth of the FR products	Usually penetration depth of the FR products of the order of 1 mm or less
Lasts more than surface treatments as long as not being exposed to outdoor weathering, but is not renewable	Requires retreatment at the end of its service life
-	Intumescent film forming
-	Susceptibility to abrasion and wear as

	a result of film formation, which result in the loss of FR efficiency

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Table 2 – Classes of active chemicals and potential mechanisms of action for common Fire Retardant (FR) for wood (adapted from Hakkarainen *et al.*, 2005; Östman *et al.,* 2006; Russell *et al.,* 2007)

Class of FR active chemicals		**Potential FR mechanisms of action**
Phosphorus compounds	Phosphoric acid; ammonium polyphosphate; (mono)ammonium (dihydrogen) phosphate; (di)ammonium (hydrogen) phosphate; poly(ammonium polyphosphate); orthophosphorous acid; monoammonium phosphate; diammonium phosphate; guanidine phosphate; phosphonates.	Changing the pathway of pyrolysis of wood; isolating surface layers (substances responsible for dehydration and esterification).
Boron compounds	Boric acid; boric oxide; boroxide; metaboric acid;	Changing the pathway of pyrolysis of wood; isolating

	borax; borax pentahydrate; borax+boric acid; sodium tetraborate (both the pentahydrate and anhydrous forms); sodium perborate tetrahydrate; sodium tetraborate x-hydrate; sodium borate+boric acid.	surface layers (substances responsible for esterification).
Nitrogen compounds	Melamine; melamine-formaldehyde resins; urea; dicyandiamide.	Isolating surface layers (substances that enhancing intumescence).
Combined phosphorus-nitrogen systems	Melamine phosphate; melamine monophosphate; guanylurea phosphate; guanyl phosphate.	Changing the pathway of pyrolysis of wood; isolating surface layers (substances responsible for dehydration and esterification and substances that enhancing intumescence).
Combined sulfur-nitrogen	Ammonium sulfate; ammonium sulfamate.	-

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systems		
Metal hydrates	Aluminium trihydroxide.	Changing the thermal properties of wood; diluting pyrolysis gases.

Table 3 – Active chemicals of Fire Retardant (FR) surface treatments for wood (adapted from Wladyka-Przybylak and Kozlowski, 1999; White and Dietenberger, 2001, 2010; Hakkarainen *et al.*, 2005; Chou *et al.,* 2009)

Fire retardant surface treatments for wood		**Active chemicals**
Intumescent treatment	**Substances responsible for dehydration**	Diammonium/monoammonium phosphates; ammonium polyphosphate; melamine phosphate; guanyl urea phosphate; urea phosphate; ammonium tetraborate.
	Substances responsible for esterification	Diammonium/monoammonium phosphate; melamine phosphate; polyphosphorylamide; tributyl phosphate; ammonium magnesium phosphate; boric acid; borax.
	Substances that enhancing intumescence	Urea; melamine; dicyandiamide; guanidine; glycine; chlorate paraffin.
	Substances	Sucrose; starch; glucose; polyhydric alcohols;

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	responsible for forming char	dipentaerythritol; maltose; arabinose; dextrin; polyhydric phenols/alcohols; rezorcinol; erythritol; pentaerythritol; dipentaerythritol; pentaerythritol dimer/trimer; arabitol; sorbitol; inositol.
Non-intumescent treatment		Diammonium phosphate; borax; ammonium sulfate.

Table 4 – Tested substrate conditions and corresponding reaction to fire tests performed

Substrate conditions			**Radiant panel test**	**SBI test**
Old wood with degradation by wood-boring beetles	With an **oily** product at the surface	**CO**	X[1]	X[1]
	After removing the oily product from the surface (**clean**)	**CL**	X[1]	X[2]
	After removing the oily product from the surface and applied an organic preservative product (**insecticide**) on the surface	**CI**	X[1]	-
New wood without biological attack	Without preservative treatment (**clean**)	**SL**	X	-
	With an organic preservative product (**insecticide**) on the surface	**SI**	X	-

[1]With wood from roof trusses.

[2]With wood from floor boards.

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Table 5 – Application procedure, solvent type and total cost/m² of the Fire Retardant (FR) treatments applied

Fire Retardant (FR) treatment		Number of coats				Total amount applied (g/m²)				Solvent		Total Cost (€/m²)
		Primer	FR undercoat	Topcoat	Total	Primer	FR undercoat	Topcoat	Total	Aqueous	Organic	
P1	Individual product	-	1	-	1	-	725	-	725	X	-	2.6
P2		-	2	-	2	-	291	-	291	X	-	3.5
P3		-	4	-	4	-	1072	-	1072	-	X	24.9
P4	Paint syste	1	1	1	3	100	300	75	475	X	X	8.5

P5	**m**	2	3	1	6	300	750	93	1143	X	X	19.9

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Table 6 – Chemical compounds of the Fire Retardant (FR) treatments studied

<table>
<tr><th colspan="3">Fire Retardant (FR) treatments</th><th>Fire retardant chemical compounds</th><th>Class of fire retardant active chemicals</th></tr>
<tr><td rowspan="3">Individual product</td><td colspan="2">P1</td><td>Urea, ammonium phosphate.</td><td>Phosphorus and Nitrogen compounds.</td></tr>
<tr><td colspan="2">P2</td><td>Ammonium polyphosphate.</td><td>Phosphorus compounds.</td></tr>
<tr><td colspan="2">P3</td><td>Ammonium polyphosphate, pentaerythritol.</td><td>Phosphorus and alcohol compounds.</td></tr>
<tr><td rowspan="3">Paint system</td><td>P4</td><td>FR undercoat</td><td>Melamine-urea-formaldehyde resins.</td><td>Nitrogen compounds.</td></tr>
<tr><td rowspan="2">P5</td><td>Primer</td><td>Ammonium polyphosphate.</td><td>Phosphorus compounds.</td></tr>
<tr><td>FR undercoat</td><td>Ammonium polyphosphate, pentaerythritol, melamine-urea-formaldehyde resins.</td><td>Phosphorus, Nitrogen and alcohol compounds.</td></tr>
</table>

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Table 7 – Fire Retardant (FR) treatments designation given by producers and ETAG 028 (2009)

Fire retardant treatment		**Fire protection given through fire retardant application**	
		According to producers	**According to ETAG 028 (2009)**
P1	**Individual product**	*Ignífugo* impregnation	Surface impregnation treatment
P2		*Ignífugo*	Surface impregnation treatment
P3		Intumescent	Intumescent
P4	**Paint system**	Intumescent	Intumescent
P5		Intumescent and *ignífugo*	Intumescent

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Table 8 – Combination of the variables studied and the nomenclature adopted

Substrate conditions	Fire retardant treatment									
	P0[(1)]	**P1**	**P2**	**P3**	**P4**[(2)]	**P5**	**P0**[(1)]	**P1**	**P4**[(3)]	**P5**
CO	COP0	COP1	COP2	COP3	COP4	COP5	COP0	COP1	COP4	COP5
CL	CLP0' CLP0''	-	-	-	-	-	CLP0	CLP1	CLP4	CLP5
CI	CIP0	CIP1	CIP2	CIP3	CIP4	CIP5	-	-	-	-
SL	SLP0' SLP0''	SLP1	SLP2	SLP3	SLP4	SLP5	-	-	-	-
SI	SIP0	-	-	-	-	-	-	-	-	-
	Radiant panel test						**SBI test**			

[(1)]Without application of any FR treatment.

[(2)]Without primer application.

[(3)]With primer application.

Table 9 – Fire retardant treatments ranking in accordance with substrate conditions tested

<table>
<tr><th colspan="2" rowspan="2">Substrate conditions</th><th colspan="3">Performance parameters (in increasing order of)</th></tr>
<tr><th>Maximum flame spread distance</th><th>Smoke production rate</th><th>Heat release rate</th></tr>
<tr><td colspan="2">New wood without biological attack</td><td>P4[(1)]<P1<P3<P5<P2</td><td>P4[(1)]<P1<P5<P2<P3</td><td>-</td></tr>
<tr><td>Old wood with attack by wood-boring beetles</td><td>After removing the oily product from the surface (clean)</td><td>-</td><td>P5<P4[(2)]<P1</td><td>P5<P1<P4[(2)]</td></tr>
</table>

	After removing the oily product from the surface and applied an organic preservative product (insecticide) on the surface	P5<P3<P1<P2<P4[(1)]	P1<P5<P2<P3<P4[(1)]	-
	With an oily product at the surface	P5<P3<P1<P4[(1)]<P2	P1<P5<P4[(1)]<P2<P3 P5<P1<P4[(2)]	P5<P1<P4[(2)]

[(1)]Without primer application.

[(2)]With primer application.

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